# NON-ISOTHERMAL DEHYDRATION KINETICS OF ACRYLIC ION-EXCHANGE RESINS

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The kinetic parameters (reaction order, $n$, activation energy, $E$, pre-exponential factor, $A$, constant rate, $k$) for the dehydration step due to elimination of osmotic water and hydrogen-bounded water with the carboxylic groups, and for the anhydrifying step owing to the dehydration of two neighboring (–COOH) groups, were determined under non-isothermal conditions for some carboxylic resins with acrylic-divinylbenzene (DVB) matrix. The kinetic parameters were evaluated by means of isoconversional methods from (TG/DTG) thermal analysis data. The results show a dependence of the apparent kinetic parameters on the cross-linking degree, granulation, gel/macroporous matrix nature, exchange capacity and heating rate.

*Keywords: acrylic ion-exchange resins, cationites dehydration, non-isothermal kinetic parameters, TG/DTG thermal analysis*

## Introduction

Frequently used in the ionic exchange field, both strong acid (with –SO₃H groups) and weak acid (with –COOH groups) cationic resins have been imposed as potential catalysts in various industrial heterogeneous processes [1–3]. The thermal stability and the water content are important characteristics of these resins when they are used as catalysts in organic, anhydrous or aqueous media [2–4].

For the strong acid cationites of polystyrene-divinylbenzene-sulphonic type, the literature offers a large set of data referring to the decomposition in non-isothermal conditions, which proves an indubitable influence of the experimental conditions and of the resins properties over the registered mass losses kinetics [5–9], for the weak acid cationites, the data are much less [10, 11].

In this context and continuing our anterior studies, this paper presents the influence of the experimental conditions and of the resins characteristics (cross-linking degree, granulation, polymeric matrix gel/macroporous nature, ionic exchange capacity and heating rate) upon the apparent kinetic parameters ($n$ – the reaction order; $E$ – the activation energy, $A$ – the pre-exponential factor, $k$ – the rate constant) afferent to the thermal process of dehydration and anhydrifying steps registered at heating under non-isothermal conditions of a series of weak acid carboxylic cationites with polymeric matrix based on acrylic acid cross-linked with divinylbenzene (DVB) (Scheme 1).
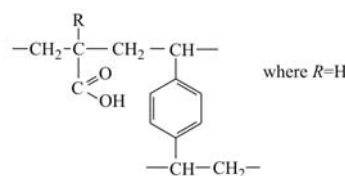


**Scheme 1**

These resins exhibit a high exchange capacity and an excellent osmotic shock resistance. They are obtained through direct copolymerization of the acrylic acid with DVB, or through hydrolysis of the resins obtained from copolymerization of some acrylic esters or even of acrylonitrile with some cross-linking agent [2, 12]. Due to their versatile properties and because they are produced with a high purity degree, the carboxylic low-acidity cationites became suitable catalysts in various food technologies [13, 14].

## Experimental

### Materials

The main physical and chemical characteristics of the investigated carboxylic cationites, made by Purolite International Ltd. – England, are reported in Table 1, together with some of producer data. From this table it can be inferred that the cross-linking degree values are between 7 and 12% DVB [12] and ion-exchange capacity is between 9.12 and 9.7 mEq g⁻¹. The ionic form for all the investigated cationites was (H⁺).

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**Table 1** The main characteristics of the investigated carboxylic cationites [12]

| No. | Cationite | Ionic form | Cross-linking degree/DVB% | Exchange capacity/mEq g$^{-1}$* | Granulation/mesh | Matrix nature |
|-----|-----------|------------|---------------------------|--------------------------------|------------------|---------------|
| 1 | Purolite C104 | H$^+$ | 10 | 9.42 | 14–20 35–50 | macroporous |
| 2 | Purolite C105 | H$^+$ | 7.2 | 9.38 | 35–50 50–60 | gel |
| 3 | Purolite C106 | H$^+$ | 12 | 9.31 | 20–30 35–50 50–60 | macroporous |
| 4 | Purolite C106EP | H$^+$ | 12 | 9.12 | 35–50 50–60 | gel |
| 5 | Purolite C107E | H$^+$ | 9 | 9.69 | 14–20 20–30 35–50 50–60 60–70 | macroporous |

*Experimentally values measured by acid-base titration.

The treatment of the commercial resin samples as well as the procedure of measuring exchange capacity for Purolite (H$^+$) cationites were described previously [4, 15, 16].

*Thermal analysis*

The thermogravimetric experiments were performed on a Perkin-Elmer TGA 7 Thermal Analysis System between 35–200 and 35–600°C using platinum crucibles.

The measurements were carried out in air flow (50 mL min$^{-1}$) at three different heating rates (β=2.5, 5 and 10 K min$^{-1}$) for granulated or grinded samples (dried at ambient temperature). The sample masses were ~2 mg.

## Results and discussion

The study of the TG/DTG curves, recorded on granulated or grinded Purolite weak-acid cationites, led to the identification of five decomposition steps associated with mass losses, which were characterized on the bases of FTIR and MS spectra analysis [11, 15–18].

The first decomposition step ($\Delta m_1$) is due to an elimination of the osmotic water, existing in the granules pores and of the hydrogen-bounded water with the carboxylic groups (–COOH). The second decomposition step ($\Delta m_2$) is due to an anhydrifying process owing to the dehydration of two neighboring (–COOH) groups which induces a cyclic poly-anhydrides formation. The third and fourth mass loss steps ($\Delta m_3$) and ($\Delta m_4$) correspond to a decarboxylation process of the polyanhydrides and to some depolymerization reaction of the polymeric matrix. The last decomposition step ($\Delta m_5$) may be associated with total degradation of the polymeric matrix and of the depolymerized fragments.

The general aspect of the TG/DTG curves recorded in air flow, between 35–650°C, is exemplified for Purolite C106 resins in granulated state (Fig. 1) and grinded state (Fig. 2).

From curves showed in Fig. 1 can be observed that for the granulated cationite the first dehydration step ($\Delta m_1$) was recorded between ~39 and ~218°C, with the
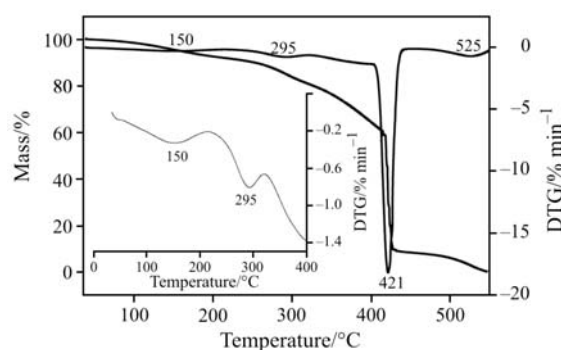


**Fig. 1** TG/DTG curves recorded in air for Purolite C106 cationites with 35–50 mesh granulation; β=5 K min$^{-1}$; *m*=2.215 mg
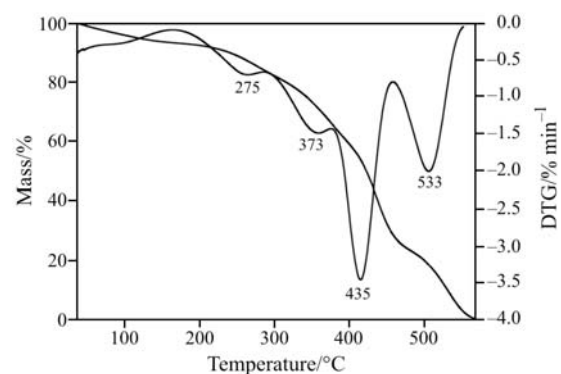


**Fig. 2** TG/DTG curves recorded in air for the grinded cationite Purolite C106, β=5 K min$^{-1}$; *m*=2.413 mg

**Table 2** Kinetic parameters dependence of the dehydration step ($\Delta m_1$) and anhydrifying step ($\Delta m_2$) upon the resins cross-linking degree of the carboxylic cationites ($\beta$=2.5 K min$^{-1}$)

| No. | Cationite | Cross-linking degree/DVB% | Granulation/ mesh | Step ($\Delta m_1$) | | | | | Step ($\Delta m_2$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ | $n$ | $r$ | $k_{413}$/s$^{-1}$ | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ | $n$ | $r$ | $k_{500}$/s$^{-1}$ |
| 1 | Purolite C105 | 7.2 | 35–50 | 40.46 | $1.8 \cdot 10^3$ | 1.6 | 0.9989 | $1.4 \cdot 10^{-2}$ | – | – | – | – | – |
| | | | grinded | – | – | – | – | – | 106.51 | $7.3 \cdot 10^9$ | 1.9 | 0.9991 | $5.4 \cdot 10^{-2}$ |
| 2 | Purolite C107E | 9 | 20–30 | 48.92 | $6.5 \cdot 10^3$ | 1.4 | 0.9992 | $4.2 \cdot 10^{-3}$ | – | – | – | – | – |
| | | | grinded | – | – | – | – | – | 111.44 | $7.6 \cdot 10^9$ | 1.7 | 0.9988 | $1.8 \cdot 10^{-2}$ |
| 3 | Purolite C104 | 10 | 14–20 | 62.48 | $5.1 \cdot 10^4$ | 1.8 | 0.9989 | $6.2 \cdot 10^{-4}$ | – | – | – | – | – |
| | | | grinded | – | – | – | – | – | 118.21 | $2.1 \cdot 10^{10}$ | 2.5 | 0.9987 | $9.2 \cdot 10^{-3}$ |
| 4 | Purolite C106 | 12 | 20–30 | 66.84 | $9.81 \cdot 10^4$ | 1.8 | 0.9994 | $3.4 \cdot 10^{-4}$ | – | – | – | – | – |
| | | | grinded | – | – | – | – | – | 120.07 | $2.98 \cdot 10^{10}$ | 2.5 | 0.9993 | $8.4 \cdot 10^{-3}$ |

DTG peak temperature value $T_{infl}=150°C$ (see also the enlargement). For the grounded cationite (Fig. 2) the anhydrifying step ($\Delta m_2$) was recorded in the temperature range ~173~298°C with the DTG peak temperature value $T_{infl}=275°C$. It can also be noticed that the first dehydration step ($\Delta m_1$) can not be totally recorded for the grounded cationite. The cationite grinding has improved the recorded curves shape on anhydrifying step ($\Delta m_2$). In order to evaluate the non-isothermal kinetic parameters for the dehydration steps ($\Delta m_1$), the recorded curves of granulated cationite has been preferred. For evaluating the non-isothermal kinetic parameters of the anhydrifying step ($\Delta m_2$), the grounded cationite use is recommended in order to record the curves [17].

For the study of the non-isothermal dehydration kinetics for acrylic ion-exchange resins, the non-isothermal kinetic parameters ($E$ – activation energy, $A$ – pre-exponential factor) corresponding to the dehydration steps ($\Delta m_1$) and anhydrifying step ($\Delta m_2$) were evaluated by means of Friedman isoconversional method (FR) based on Eq. (1) [17, 19].

$$\ln \frac{d\alpha}{dt} = \ln Af(\alpha) - \frac{E}{RT} \quad (1)$$

In order to find out the analytical form of the conversion function $f(\alpha)$ and the value of reaction order, $n$, the method suggested by Tanaka and Koga [17, 20] based on the kinetic compensation effect, was used.

The constant rate values, $k$, were determined using the Arrhenius equation, Eq. (2).

$$k(T) = Ae^{-E/RT} \quad (2)$$

where $k(T)$ – constant rate, $\alpha$ – degree of conversion, $f(\alpha)$ – differential conversion factor, $A$ – pre-exponential factor, $E$ – activation energy and $R$ – general gas constant.

*Effect of the cross-linking degree*

Table 2 presents the effect of the degree of cross-linking on the kinetics of dehydration step ($\Delta m_1$) and anhydrifying step ($\Delta m_2$) for the investigated cationites.

From Table 2 data results that for both mass loss steps, the values of the pre-exponential factor are increasing with the increase of the cross-linking degree

from 7.2% DVB to 12% DVB, partially compensating the increase of the activation energy in the same order. Thus for the dehydration step ($\Delta m_1$) the pre-exponential factor, $A$, varies from ~$1.4 \cdot 10^3$ to ~$9 \cdot 10^4$ $s^{-1}$ and for the anhydrifying step ($\Delta m_2$) from ~$7 \cdot 10^9$ to ~$2 \cdot 10^{10}$ $s^{-1}$. The values of the apparent kinetic constants, $k_{413}$ and $k_{500}$, calculated on the base of $E$ and $A$ are decreasing with the increase of the cross-linking degree from $1.4 \cdot 10^{-2}$ to $3.4 \cdot 10^{-4}$ $s^{-1}$ for the first step and from $5.4 \cdot 10^{-2}$ to $8.4 \cdot 10^{-3}$ $s^{-1}$ for the second decomposition step. A possible explanation of this behaviour is that, with the increase of the cross-linking degree, the resin inflexibility also increases [2, 5], which in turn limits the possibility of free rotation and 'relative accommodation' [21] of the polymeric chains and of the carboxylic functional groups. Because of this, both, the neighboring –COOH groups and the water molecules attached to them by hydrogen bonds, are forced to a more vigorous interactions.

Probably this phenomenon is responsible for the observed increase of the activation energy, $E$ and of the reaction order, $n$, with the growth of cross-linking degree.

A similar behavior has been presented in the literature for the dehydration of the strong acid resins polystyrene-DVB type [5, 22].

The results in Table 2 suggests an improvement of the thermal stability with increase of the reticulate percent.

*Effect of gel/macroporous matrix nature*

The influence of the polymeric matrix nature on the apparent kinetic parameters due to the dehydration step ($\Delta m_1$) of cationites is presented in Table 3.

From Table 3 it can be noticed that in the case of an equal (DVB%) content, the passing from the gel nature matrix to the macroporous one caused a diminishing of the kinetic parameters. Thus the activation energy, $E$, decreases from 54.25 to 42.74 kJ mol$^{-1}$ and the pre-exponential factor, $A$, from $5.3 \cdot 10^3$ to $1.1 \cdot 10^2$ $s^{-1}$. Regarding the values of the apparent rate constant, $k$, these are also increasing with about one order of magnitude (from $7.2 \cdot 10^{-4}$ to $4.2 \cdot 10^{-3}$ $s^{-1}$) as passing from the gel form to the macroporous form. These results may suggest a possible overlapping of the diffusion on

**Table 3** Kinetic parameters dependence of the dehydration step ($\Delta m_1$) upon the gel/macroporous matrix nature ($\beta$=10 K min$^{-1}$, granulation 50–60 mesh)

| No. | Cationite | Matrix nature | Step ($\Delta m_1$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ | $n$ | $r$ | $k_{413}$/s$^{-1}$ |
| 1 | Purolite C106EP 12% DVB | gel | 54.25 | $5.3 \cdot 10^3$ | 1.6 | 0.998 | $7.2 \cdot 10^{-4}$ |
| 2 | Purolite C106 12% DVB | macroporous | 42.74 | $1.1 \cdot 10^2$ | 1.8 | 0.999 | $4.22 \cdot 10^{-3}$ |

**Table 4** The granulation influence on the dehydration step ($\Delta m_1$) kinetic for the Purolite C107E cationite, $\beta=5$ K min$^{-1}$

| No. | Cationite | Granulation/mesh | Step ($\Delta m_1$) | | | | |
|---|---|---|---|---|---|---|---|
| | | | $E$/kJ mol$^{-1}$ | $A$/s$^{-1}$ | $n$ | $r$ | $k_{413}$/s$^{-1}$ |
| 1 | | 14–20 | 57.24 | $8.1 \cdot 10^4$ | 1.4 | 0.998 | $4.6 \cdot 10^{-3}$ |
| 2 | | 30–35 | 50.04 | $1.4 \cdot 10^4$ | 1.4 | 0.998 | $6.5 \cdot 10^{-3}$ |
| 3 | Purolite C107E | 35–50 | 45.22 | $1.1 \cdot 10^4$ | 1.3 | 0.999 | $2.2 \cdot 10^{-2}$ |
| 4 | | 50–60 | 42.11 | $6.6 \cdot 10^3$ | 1.4 | 0.997 | $3.1 \cdot 10^{-2}$ |
| 5 | | 60–70 | 36.24 | $2.3 \cdot 10^2$ | 1.3 | 0.999 | $6.8 \cdot 10^{-2}$ |

the dehydration process which takes place. This overlapping becomes significant in the case of the gel type polymeric matrix with smaller porosity.

The anhydrifying step ($\Delta m_2$), studied for grinded resins, the transition from the gel form to the macroporous form did not, significantly, influenced the values of the kinetic parameters. This result is probably due to the grinding procedure which partially destroys the macroporous structure.

*Effect of granulation*

The influence of the cationites granulation upon the kinetic parameters of the dehydration step ($\Delta m_1$) is presented in Table 4 for macroporous resin for which the TG curves, at air, are shown in Fig. 3.

Figure 3 shows a displacement of the TG curves, on the temperature axe, to higher values as sample granulation increases. In accordance with the TG measurements, the data from Table 4 presents a decrease of kinetic parameters $E$ and $A$, and an increase of the apparent kinetic constant, $k$, as diameters of cationite granules are reducing.

Even if the increased values of the kinetic constants $k_{413}$ from Table 4 and the position of the TG curves from Fig. 3 may suggest an increase of the cationites thermal stability with the increas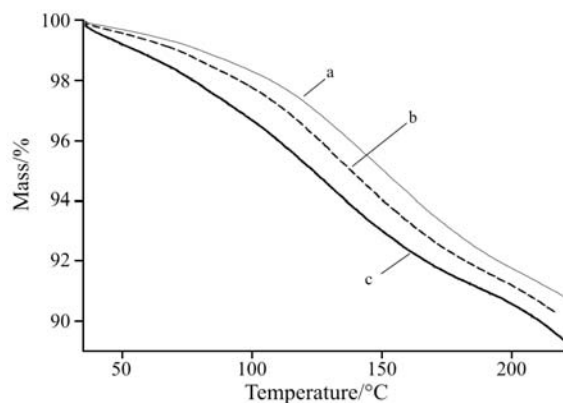e of the granulation, a more plausible explanation of the obtained results is that, on one side the small diameter granules insure an improve of the sample thermal conductivity, and on the other side, the contact surface of these granules with the crucible and the surrounding medium is better. Under these conditions the heat exchange is faster and the temperature measured by the thermocouple is closer to the samples real one. Also with small granulation samples, the external contact surface with decomposition medium is higher, and so the elimination of the volatile compounds is easier and therefore is diminished the overlapping effect of the diffusion on the dehydration process.

*Effect of the heating rate*

The influence of the heating rate on the kinetics of dehydration step ($\Delta m_1$) and of anhydrifying step ($\Delta m_2$), for carboxylic cationites is shown in Table 5.

As it can be noticed from Table 5, the increase of the heating rate led to the decrease of the non-isothermal kinetic parameters $E$ and $A$, for both decomposition steps. For example, for the Purolite C106 cationite, with the heating rate increase the activation energy decreases about 1.3 times for ($\Delta m_1$) and about 1.1 times for ($\Delta m_2$) (also Table 2). Also, the values of pre-exponential factor, $A$, diminishing, respectively about 15.3 times for ($\Delta m_1$) and about 6 times for ($\Delta m_2$). The values of reaction constants $k_{413}$ are not significantly influenced by the heating rate changes.

The dependence of the non-isothermal kinetic parameters on the heating rate reveals in any way the complexity of the phenomena that are taking place during the two mass loss steps. In our opinion, the dehydrating processes and the diffusion one are proceeding simultaneously and are influencing each other. The competition between the two processes can explain the noticed variation of the kinetic parameters with the heating rate.

On the other side, the obtained results prove that, in case of a higher heating rate, the elimination of the hydration water from the cationite is easier. If the values of the heating rate are small, the latest water molecules are more difficult to eliminate because there are more powerful anchored, in the matrix of the hydrogen bonds, with the carboxylic functional groups [5, 6].



**Fig. 3** TG curves recorded in air for the macroporous cationite Purolite C107E with the granulation a – 20–30 mesh, b – 35–50 mesh and c – 60–70 mesh; $\beta=5$ K min$^{-1}$

**Table 5** The influence of the heating rate β on the kinetic of the cationites decomposition steps ($\Delta m_1$) and ($\Delta m_2$)

| No. | Cationite (H⁺) | $\beta$/K min⁻¹ | Step ($\Delta m_1$)* | | | | | Step ($\Delta m_2$)** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $E$/kJ mol⁻¹ | $A$/s⁻¹ | $n$ | $r$ | $k_{413}$/s⁻¹ | $E$/kJ mol⁻¹ | $A$/s⁻¹ | $n$ | $r$ | $k_{500}$/s⁻¹ |
| 1 | Purolite C104 | 2.5 | 58.12 | $9.1 \cdot 10^4$ | 1.7 | 0.9989 | $3.9 \cdot 10^{-3}$ | – | – | – | – | – |
| 2 | | 5 | 51.22 | $1.2 \cdot 10^4$ | 1.6 | 0.9998 | $4.1 \cdot 10^{-3}$ | 110.47 | $2.8 \cdot 10^9$ | 2.6 | 0.9992 | $8.1 \cdot 10^{-3}$ |
| 3 | | 10 | 38.11 | $4.8 \cdot 10^3$ | 1.6 | 0.9992 | $7.2 \cdot 10^{-2}$ | 100.84 | $1.2 \cdot 10^9$ | 2.5 | 0.9989 | $3.5 \cdot 10^{-2}$ |
| 4 | Purolite C106 | 2.5 | 60.21 | $3.4 \cdot 10^4$ | 1.8 | 0.9987 | $8.2 \cdot 10^{-3}$ | – | – | – | – | – |
| 5 | | 5 | 58.89 | $2.9 \cdot 10^4$ | 1.7 | 0.9989 | $1.1 \cdot 10^{-3}$ | 117.21 | $1.3 \cdot 10^{10}$ | 2.4 | 0.9989 | $7.6 \cdot 10^{-3}$ |
| 6 | | 10 | 47.21 | $5.2 \cdot 10^3$ | 1.8 | 0.9991 | $5.6 \cdot 10^{-3}$ | 106.85 | $1.8 \cdot 10^9$ | 2.3 | 0.9994 | $1.2 \cdot 10^{-2}$ |

*sample granulation 35–50 mesh; **grinded sample

These observations are also according with Zundel's findings for the dehydration kinetic of some strong acid cationites with –SO$_3$H groups [23].

## Conclusions

The kinetics of the non-isothermal dehydration of some acrylic ion-exchange resins was studied. The value of kinetic parameters (reaction order, $n$, activation energy, $E$, pre-exponential factor, $A$, constant rate, $k$) for the dehydration step due to elimination of osmotic water and hydrogen-bounded water with the carboxylic groups and for the anhydrifying step by the dehydration of two neighboring (–COOH) groups, were calculated by means (FR) isoconversional method. The results revealed a strong influence of the experimental parameters (heating rate) as well as of the resins characteristics (cross-linking degree, granulation, gel/macroporous matrix nature, exchange capacity) upon the kinetics of dehydration and anhydrifying steps. A superposition of a diffusion process over the chemical process investigated has been noticed.

## Acknowledgements

## References

1 M. Marhol, 'Comprehensive Analytical Chemistry', Vol. XIV, Ion Exchangers, 1982, pp. 117–160.

2 F. Helfferich, 'Ion Exchange', McGraw-Hill, New York 1962, p. 519.

3 W. Neier, 'Ion Exchangers', K. Dorfner, Ed., Walter der Gruyte, 1991, p. 1016.

4 C. Idiţoiu, E. Segal and D. Chambre, J. Therm. Anal. Cal., 56 (1999) 407.

5 C. Idiţoiu and E. Segal, Rev. Chim., 5 (1980) 473.

6 C. Idiţoiu, C. Popescu and D. Chambre, J. Therm. Anal. Cal., 55 (1998) 885.

7 M. Matsuda, K. Funabashi and T. Nishi, Nucl. Technol., 75 (1986) 187.

8 M. Matsuda, K. Funabashi and H. Yusa, J. Nucl. Sci. Technol., 24 (1987) 124.

9 S. Petterson and G. Kemmler, Waste Manage., 84 (1986) 223.

10 I. C. McNeill and S. M. T. Sadeghi, Polym. Degrad. Stab., 29 (1990) 233.

11 D. Chambre, C. Idiţoiu, E. Segal and A. Cesàro, J. Therm. Anal. Cal., 82 (2005) 803.

12 'Ion Exchange Resins', Purolite Co., Tehnical Book, UK 1998.

13 E. Dickinson and G. Stanisly, 'Colloids and Foods', Appl. Sci. Publ., London–New York 1982, p. 220.

14 D. Chambre, C. Idiţoiu, E. Segal and M. R. Szabo, Annals of West University of Timisoara, Series Chemistry, 12 (2003) 1591.

15 C. Idiţoiu, D. Chambre and R. M. Siladi, Sci. Tech. Bull., Univ. Arad, 5 (2000) 1.

16 D. Chambre, C. Idiţoiu and M. R. Szabo, Sci. Tech. Bull., Univ., Arad, 10 (2005) 43.

17 D. Chambre, C. Idiţoiu, P. Budrugeac and E. Segal, Rev. Chim. (Bucureşti), 56 (2005) 502.

18 G. C. Eastmond, Comprehensive Polym. Sci., Polym. Reactions, Vol. 6, Pergamon Press, 1989, p. 461.

19 H. L. Friedman, J. Polym. Sci., 50 (1965) 13.

20 H. Tanaka and N. Koga, J. Thermal Anal., 34 (1988) 685.

21 J. A. Marinsky, 'Ion Exchange', Vol. 2, Ed. M. Dekker Inc., NY 1969, p. 354.

22 C. Idiţoiu and E. Segal, Rev. Chim., 6 (1980) 546.

23 G. Zundel, 'Titration and Intermolecular Interaction', Academic Press, NY 1970, p. 172.